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A WATER-DISPERSIBLE RESIN COMPOSITION

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[Translator's note: The attached requested amendments are incorporated into the text of this translation.]

Specification

1. Title of the invention

A water-dispersible resin composition

2. Claims of the invention

1. An emulsion prepared by polymerizing (a) α, β -monoethylenic unsaturated carboxylic acid amide, and (or) substitutents thereof, having at least one N-substituted methylol group, (b) a colloidal silica and (c) a polymeric organic monomer other than the above-mentioned (a) which is copolymerizable with the above-mentioned components, in which water-dispersible resin composition an adjustment is made to produce a ratio of the parts solids by weight of (a):(b):(c) in the range of 100:0.1-20:1-200,

and a polymerization initiator, in which a trace amount of a transition metal ion is included as an accelerator, is used so as to form particles with a mean particle diameter in the range of 0.01~0.08 μm .

2. The water-dispersible resin composition described in Claim 1, in which (d) an amino resin and (or) an epoxy resin also is added.

3. Detailed explanation of the invention

[Objective of the invention]

[field of industrial application]

The present invention pertains to a water-dispersible resin composition capable of forming a film having excellent properties such as high flame retardancy, solvent resistance, blocking resistance, heat resistance, transparency, water resistance, soil resistance, and corrosion resistance.

[Prior art]

In recent years, from the standpoint of environmental pollution and safety and sanitation, use of water-based paint is promoted and conventional solvent type paints are being replaced by aqueous emulsion paints. Under the circumstances, a high coating formability is required for the paint emulsion, and an increase in the wear resistance of the coating is essential. In the past, as a method for producing an aqueous dispersion of a resin, emulsion polymerization has been used and for increasing the stability of the resulting dispersion, many different types

of surfactants and water-soluble polymer materials can be used independently or in the form of a mixture. However, when an emulsifier based on a surfactant is used, *//illegible//* resistance is likely to be inadequate due to the activating agent included; on the other hand, in a method wherein a water-soluble polymer material such as methyl cellulose and polyvinyl alcohol is used, in general, it is not possible to produce a stable dispersion of the resin; furthermore, even when it is possible, the water resistance and flexibility of the resin produced are inadequate; thus, practical application has not been possible.

[p. 2]

As a method of eliminating the above-mentioned problem points, the invention described in Japanese Kokai Patent Application No. Sho 49-4739 was previously submitted by the present inventors. According to the invention, adequate water resistance can be obtained. However, the most important factor concerning the emulsion paint is a significant increase in wear resistance so that a hard film with a good film formability can be achieved. In order to achieve the objective, many suggestions have been made in the past.

As one method that has been suggested, a method that can be mentioned is one in which a film-forming coagent is added to a polymeric emulsion having a relatively high Tg value. In that method, it is necessary to take the stability and volatility of the polymeric emulsion into consideration, and selection is very difficult. Furthermore, a multi-stage polymerization process has

been suggested. In this case, the emulsion has a polymeric composition in which a core having a high Tg value and a shell having a relatively low Tg value is produced. In that method, the desired properties can be effectively achieved when the amount of emulsifier used for the polymerization is relatively low, but when the product is used as a paint, additional emulsifier and water-soluble resin are required to increase the stability of the paint; furthermore, the water resistance is very poor, and deterioration in the properties with time occurs. Furthermore, a method wherein a polymeric emulsion with a high Tg value and a polymeric emulsion with a low Tg value are blended apart from the above-mentioned multi-stage polymerization process has been suggested, but the solubility of emulsions is inadequate and the wear resistance of the coated film remains inadequate.

As described above, a paint in which an organic polymer alone is used is limited, and a blend of an inorganic silica, an organic polymer or the reaction product of these materials has been suggested. For example, a method in which a colloidal silica is used as the inorganic silica and an organic polymer is blended has been suggested to increase the wear resistance, flame retardancy, and blocking resistance. However, bonding between the inorganic silica and organic polymer is insufficient when the above method is used and deterioration in the coated film eventually occurs. Thus, as a method of reducing the above-mentioned disadvantages, use of alkoxy silanes in combination has

been suggested. However, the long-term storage properties are inadequate when the above-mentioned method is used.

Meanwhile, as a means to eliminate the above-mentioned disadvantages, a method wherein emulsion copolymerization is carried out with different monomers in a single-stage polymerization with a monomer having a polymeric unsaturated double-bond containing an alkoxy silane group has been suggested. However, when the above-mentioned method is used, the elongation of the coated film produced is inadequate and the proportion of coagulants produced during the emulsion copolymerization is high, and the method is inefficient. As a result, a high proportion of an emulsifier is required and as a result, the water resistance and other properties are significantly poorer.

As described above, it has been confirmed that use of an alkoxy silane is effective for increasing the mutual bonding between an inorganic silica and organic polymer, but many problems remain unsolved.

[Problems to be solved by the invention]

As a result of much research carried out by the present inventors, when a water-dispersible resin composition having particles with a mean diameter in the range of 0.01-0.08 μm produced by emulsion polymerization of (a) α, β -monoethylenic unsaturated carboxylic acid amide and (or) substituents thereof having at least one N-substituted methylol group, (b) colloidal silica and (c) a polymeric organic monomer other than the above-

mentioned (a) but which is copolymerizable with the above-mentioned components, with a trace amount of a transition metal ion used as an accelerator included, is used, bonding of the silica with an α,β -monoethylenic unsaturated carboxylic acid amide and/or organic polymer containing a derivative thereof in the molecule, in particular, an acrylic copolymer, can be easily achieved, and a composite of silica and an acrylic copolymer can be produced in a solution state, and an excellent gloss and high water resistance of the coated film can be achieved based on a fine particles, and as a result, the present invention was accomplished. The present invention is a reduction in the above-mentioned many existing problems and to provide a new type of industrial coating material having the advantages of organic polymers such as good film formability and flexibility and the advantages of inorganic silica, such as high hardness, solvent resistance and flame retardancy.

[Structure of the invention]

[Means to solve the problem]

The present invention is a water-dispersible resin composition produced upon emulsion polymerization of (a) α,β -monoethylenic unsaturated carboxylic acid amide and (or) a substituent thereof having at least one N-substituted methylol group, (b) colloidal silica and (c) a polymeric organic monomer other than the above-mentioned (a) but which is copolymerizable with the above-mentioned components, a water-dispersible resin composition wherein an adjustment is made to form a weight ratio

of the parts solids of (a):(b):(c) in the range of 100:0.1~20:1~200, and a polymerization initiator, wherein a trace amount of a transition metal ion is included as an accelerator, is used, so as to form particles with a mean particle diameter in the range of 0.01~0.08 μm .

[p. 3]

In this case, as polymeric organic monomers, those listed below can be used and in general, from the standpoint of enhancement of properties and application objective, monomers are used in a form of a mixture.

Alkyl (carbon atoms of 1-22) esters of acrylic acid: for example, methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethyl hexyl acrylate, lauryl acrylate, etc. Alkyl (carbon atoms of 1-22) esters of acrylic acid: for example, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, 2-ethyl hexyl methacrylate, lauryl methacrylate, etc. Vinyl monomers containing a hydroxyl group: hydroxy ethyl methacrylate, hydroxy ethyl acrylate, hydroxy propyl methacrylate, hydroxy propyl acrylate, etc.

Vinyl monomers containing a carboxyl group: for example, acrylic acid, methacrylic acid, maleic acid, maleic anhydride, itaconic acid, fumaric acid, crotonic acid, etc.

Monomers containing an amino group: For example, acryl amide, methacryl amide, allyl amine, N-isopropyl acryl amide, N,N-dimethyl ethyl methacrylate, N,N-diethyl ethyl methacrylate, etc.

Monomers containing an epoxy group: for example, clycidyl acrylate, clycidyl methacrylate, methyl clycidyl acrylate, etc.

Monomers containing an aldehyde group: for example, acrolein, etc.

Other vinyl monomers: For example, strength, vinyl toluene, acrylonitrile, vinyl chloride, vinyl acetate, vinylidene chloride, fluoro(meth)acrylate, silicon (meth)acrylate, etc. can be mentioned.

For examples of α, β -monoethylenic unsaturated carboxylic acid amide having at least one N-substituted methylol group, N-methylol acryl amide, N-methylol methacryl amide and N-dimethylol methacryl amide can be mentioned, and for derivatives thereof, N-n-butoxy methyl acrylamide, N-n-butoxy methyl methacrylamide, N-ethoxy methyl acrylamide, N-ethoxy methyl methacrylamide, N-methoxy methyl acrylamide, N-methoxy methyl methacrylamide, etc. can be mentioned.

For the colloidal silica, those commonly used in a form of an aqueous dispersing material with a primary particle diameter in the range of 5-100 nm [amendments, see p. 9] and is produced by removal of sodium from a water glass (deionized method, acid decomposition method, decomposition method, etc.) can be used in this case as well. The above-mentioned colloidal silica can be used in an acid side or an alkali side in a form of an aqueous dispersion, and for colloidal silica used in an acid side, non-stabilized silica marketed under product names such as Snow-tex O and Snow-tex OL (product of Nitto Chemical Ind. (Ltd.)) can be

used. Furthermore, for colloidal silica used in an alkali side, a stabilized colloidal silica (pH 8.4-10) upon addition of a trace amount of alkali metal ion, aluminum ion, ammonium ion or amine, can be mentioned, and those known by product names such as Snow-tex 20, Snow-tex C and Snow-tex N (product of Nitto Chemical Ind. (Ltd.)) can be used.

Furthermore, upon performing an emulsion copolymerization for the above-mentioned monomer (a) and monomer (b) and colloidal silica (c), a conventional method can be used in this case as well, and in this case, conventional anionic surfactant or nonionic surfactant can be used for the polymerization emulsifier, and in general, the amount used is in the range of approximately 0.1-10 wt% for the total amount of the organic monomer. When an excess amount is used, it is not desirable from the standpoint of properties such as water resistance, but it is not especially limited. For examples; of anionic surfactants, alcohol sulfates such as sodium lauryl sulfonate, alkyl allyl sulfonates such as dodecyl benzene sodium sulfonate, etc. can be mentioned. Furthermore, dialkyl sulfosuccinate, alkyl naphthalene sulfonate, polyoxy ethylene alkyl ether sulfate, naphthalene sulfonic acid formalin condensate, phosphate of polyoxyethylene alkyl ether, α -olefin sulfonate, etc. can be mentioned.

[p. 4]

For nonionic surfactants, polyoxyethylene alkyl phenyl ether, polyoxyethylene alkyl ether, sorbitan fatty acid ester,

polyoxyethylene sorbitan fatty acid ester, polyoxyethylene fatty acid ester, glycerol fatty acid ester, polyoxyethylene polyoxy propylene block copolymers, etc. can be mentioned.

For polymerization initiators, persulfate can be used independently, a mixture of a standard persulfate and a reducing agent, or a mixture of an organic peroxide and a reducing agent, can be used. Furthermore, in order to produce a transparency fine particles emulsion, it is essential to add a transition metal ion such as divalent copper ion in an amount of 2.5×10^{-7} - 2×10^{-2} mol/l as a polymerization accelerator.

The polymerization temperature varies depending on the polymerization initiator and the cloud point of the nonionic emulsifier, and when the above-mentioned temperature is 80°C or above, the stability of the polymer emulsion becomes inadequate, and the size of the particle diameter is likely to increase and it is not desirable. Furthermore, because the present invention is a fine particles, the viscosity increases significantly when the ratio of the non-volatile component exceeds 30%. For this reason, it is effective for reduction of the viscosity when a small amount of electrolyte (diammonium phosphate, sodium hydrogen carbonate, sodium citrate, etc.) is added.

Furthermore, the copolymerization ratio of the above-mentioned monomer (a), monomer (b) and monomer (c) is in the range of 100:0.1-20:1-200 in terms of the solid parts weight ratio, and in the range of 100:0.5-10:1-100 is further desirable. When the amount of monomer (b) is 0.1 parts by weight or below

for 100 parts by weight of the monomer (a), the reaction with the OH group on the surface of the colloidal silica (c) becomes inadequate, and wear resistance of the coated film becomes inadequate, and on the other hand, when the amount of monomer (b) is 20 parts by weight or above, the reaction progresses excessively and the target water-dispersible material cannot be produced stably. On the other hand, when the monomer (c) used is 1 parts by weight or below for 100 parts by weight of monomer (a), a firm bond of organic-inorganic materials cannot be achieved and the wear resistance of the coated film becomes inadequate, and when 200 parts by weight or more is used, coated film properties become inadequate and cracking occurs and as a result, the wear resistance of the coated film is reduced.

The water-dispersible resin composition of the present invention is mainly consisting of a composite resin produced as described above, and an amino resin and(or) epoxy resin can be further mixed, as needed. The above-mentioned additional resin behaves as a crosslinking agent, curing occurs as a result of dehydration and condensation reaction or adduct reaction with the functional group left behind the composite resin and forms a strong coated film and high water resistance, alkali resistance, acid resistance and solvent resistance can be imparted. For the above-mentioned amino resins, a known urea-formaldehyde polycondensate modified with a monohydric alcohol such as methanol and butanol, monomeric or polymeric melamine resin, benzoquanamine resin, etc. can be mentioned. Furthermore,

crosslinking of epoxy resin occurs through adduct reaction of the epoxy group included in the molecule and carboxyl group or amine group of the composite resin, and a firm film can be produced. For the above-mentioned epoxy resin, polyphenol glycidyl ethers having a mean molecular weight of approximately at least 350, preferably approximately in the range of 350-3000 and epoxy equivalent in the range of 150-3000, preferably in the range of 200-2000 can be mentioned. The mixing ratio of the above-mentioned amino resin and(or) epoxy resin and composite resin is in the range of 40/60-5/95 in terms of the weight ratio, and in the range of 30/70-10/90 is further desirable. In the case of when the amount of the above-mentioned amino resin and/or epoxy resin used exceeds the upper limit of the above-mentioned range, properties of the basic composite resin cannot be fully achieved, and on the other hand, when the amount used is below the lower limit of the above-mentioned range, the effect of the crosslinking agent is not adequate.

Additives such as pigments, fillers, plasticizers, pigments dispersants, solvents, thickeners, preservatives, defoaming agents, and leveling agents can be further included in the composition of the present invention, as needed.

The composition of the present invention can be coated onto a plastic base material, metal, paper, cloth and inorganic materials. It is especially effective when coated onto a metal or inorganic material. The silica composite water-dispersible resin composition produced as described above is transparency and

highly flexibility, and good coated film formability and flexibility of organic polymer and high hardness, solvent resistance and flame retardancy of inorganic material can be fully utilized and a new type of an industrial coating material can be produced.

[Work of the invention]

An excellent coated film achieved through the composition of the present invention is not well understood, but it is hypothesized that a reaction occurs between the OH group included on the surface of the silica, an α,β -monoethylenic unsaturated carboxylic acid amide having at least one N-substituted methylol group, and/or the derivatives thereof during the emulsion polymerization reaction and a firm crosslinking bond is produced, and when coated onto a metal base and a heat treatment is performed, a reaction occurs between the residual OH group on the surface of the colloidal silica and the OH group on the surface of the inorganic material occurs at the same time, and a firm organic-inorganic complex bond can be produced.

[p. 5]

When a polymerization initiator containing a trace amount of transition metal ion is included, the particles size of the particles produced is reduced, and the adhesion and perm; for the coating objective increase. Furthermore, (d) behaves as a crosslinking agent, and undergoes a crosslinking reaction as a result of dehydration and condensation reaction or adduct reaction with the functional group left behind the copolymer

consisting of components (a), (b) and (c) and forms a strong film, and properties such as water resistance, alkali resistance, acid resistance, solvent resistance and corrosion resistance can be further increased. Furthermore, when coated onto an inorganic base material, adhesion can be significantly increased and because of a fine particles, good permeation can be achieved for porous inorganic materials and an excellent coated film can be produced.

Application examples are shown below. In this case, parts means parts by weight in all cases.

Application example 1

- (1) Ammonium phosphate of polyoxyethylene (17 mol adduct) alkyl ether 2 parts
- (2) α -olefin sodium sulfonate 0.5 parts
- (3) Copper sulfate solution (2×10^{-4} mol/l) 100 parts
- (4) Methyl methacrylate 134 parts
- (5) Ethyl acrylate 134 parts
- (6) N-methylol acryl amide 6 parts
- (7) Ammonium phosphate of polyoxyethylene (17 mol adduct) alkyl ether 4 parts
- (8) α -olefin sodium sulfonate 1.5 parts
- (9) Ludox AM (solid parts=30%) 60 parts
- (10) Copper sulfate solution (2×10^{-5} mol/l) 461.5 parts
- (11) Diammonium phosphate 0.5 parts
- (12) 5% potassium persulfate (copper sulfate 2×10^{-5} mol/l solution) 20 parts

(13) 2% sodium bisulfite (copper sulfate 2×10^{-5} mol/l solution) 20 parts

Components (7)-(11) were charged to a reaction vessel saturated with a nitrogen gas ahead of time, heating was performed to 60°C, and emulsion monomer mixture of (1)-(6) and components (12) and (13) were dropwise added to the reaction vessel in 3 hours. The polymerization temperature used was in the range of 60°C-70°C. After addition, ageing was performed for approximately 2 hours and an adjustment was made to form the solid parts of 30% so as to produce a stable silica composite water-dispersible resin composition. The mean particle diameter (note 1) was 0.061 μm . Furthermore, an adjustment was made for the non-volatile material to form 15% and coating was performed for a calcium silicate plate at a ratio of approximately 100 g/m², and drying was performed under 100°C x 10 min, and coating was performed with a commercial water-dispersible paint to form a thickness of 1 mm and drying was subsequently performed at room temperature for approximately 14 days. When measurement was performed for the adhesion, destruction of the main component occurs at above 25 kg/cm and a very high adhesion was achieved. Note 1: Measurement was performed by Nanosizer (Product of Coulter Counter Co.)

Application example 2

(1) polyoxyethylene (17 mol adduct) nonyl ether Ammonium sulfate
2 parts

(2) polyoxyethylene (20 mol adduct) nonyl phenyl ether 0.5

parts

- (3) Copper sulfate solution (2×10^{-4} mol/l) 100 parts
- (4) Methyl methacrylate 180 parts
- (5) 2-Ethyl hexyl acrylate 126 parts
- (6) 2,2,2-trifluoroethylene methacrylate 10 parts
- (7) N-methylol acryl amide 6 parts
- (8) Acrylic acid 3 parts
- (9) polyoxyethylene (6 mol adduct) nonyl ether Ammonium sulfate 6

parts

- (10) polyoxyethylene (20 mol adduct) nonyl phenyl ether 1.5

parts

- (11) Ludox AM (solid parts=30%) 260 parts
- (12) Copper sulfate solution (2×10^{-4} mol/l) 297 parts
- (13) Diammonium phosphate 0.5 parts
- (14) 5% ammonium persulfate (copper sulfate 2×10^{-4} mol/l solution) 20 parts
- (15) 2% sodium bisulfite (copper sulfate 2×10^{-4} mol/l solution) 20 parts

Components (9)-(13) were charged to a reaction vessel saturated with a nitrogen gas ahead of time, heating was performed to 60°C, and emulsion monomer mixture of (1)-(8) and components (14) and (15) were dropwise added to the reaction vessel in 3 hours. The polymerization temperature used was in the range of 60°C-70°C. After addition, ageing was performed for approximately 2 hours and then, cooling was further performed and an adjustment was made to form the pH in the range of 8-9 with an

aqueous ammonia, and the solid parts of 40% so as to produce a stable silica composite water-dispersible resin composition. The mean particle diameter was 0.075 μm .

[p. 6]

Furthermore, an adjustment was made for the non-volatile material to form 15% and coating was performed for a calcium silicate plate at a ratio of approximately 100 g/m², and drying was performed under 100°C x 10 min, and coating was performed with a commercial water-dispersible paint to form a thickness of 1 mm and drying was subsequently performed at room temperature for approximately 14 days. When measurement was performed for the adhesion, destruction of the main component occurs at above 25 kg/cm and a very high adhesion was achieved.

Application example 3

- (1) Dioctyl sulfosuccinate 6 parts
- (2) α -olefin sodium sulfonate 3 parts
- (3) Copper sulfate solution (2 x 10⁻⁷ mol/l) 646 parts
- (4) Ludox AM (solid parts=30%) 20 parts
- (5) Butyl methacrylate 270 parts
- (6) FM0711 (note 2) 10 parts
- (7) N-n-butoxy methyl acryl amide 5 parts
- (8) 5% potassium persulfate (copper sulfate 2 x 10⁻⁷ mol/l solution) 20 parts
- (9) 2% sodium bisulfite (copper sulfate 2 x 10⁻⁷ mol/l solution) 20 parts

Components (1)-(4) were charged to a reaction vessel

saturated with a nitrogen gas ahead of time, heating was performed to 60°C, and emulsion monomer mixture of (5)-(7) and components (8) and (9) were dropwise added to the reaction vessel in 3 hours. The polymerization temperature used was in the range of 60°C-70°C. After addition, ageing was performed for approximately 2 hours and an adjustment was made to form the solid parts of 30% so as to produce a stable silica composite water-dispersible resin composition. The mean particle diameter was 0.052 μm . Furthermore, an adjustment was made for the non-volatile material to form 15% and coating was performed for a calcium silicate plate at a ratio of approximately 100 g/m², and drying was performed under 100°C x 10 min, and coating was performed with a commercial water-dispersible paint to form a thickness of 1 mm and drying was subsequently performed at room temperature for approximately 14 days. When measurement was performed for the adhesion, destruction of the main component occurs at above 25 kg/cm and a very high adhesion was achieved.

Note 2: Silicon methacrylate (product of Chisso Corp.)

Application example 4

- (1) Dioctyl sulfosuccinate 6 parts
- (2) α -olefin sodium sulfonate 3 parts
- (3) Copper sulfate solution (2×10^{-7} mol/l) 625 parts
- (4) Ludox AM (solid parts=30%) 50 parts
- (5) Butyl methacrylate 261 parts
- (6) FM0711 (note 2) 10 parts
- (7) N-n-butoxy methyl acryl amide 5 parts

(8) 5% potassium persulfate (copper sulfate 2×10^{-7} mol/l solution) 20 parts

(9) 2% sodium bisulfite (copper sulfate 2×10^{-7} mol/l solution) 20 parts

Components (1)-(4) were charged to a reaction vessel saturated with a nitrogen gas ahead of time, heating was performed to 60°C , and emulsion monomer mixture of (5)-(7) and components (8) and (9) were dropwise added to the reaction vessel in 3 hours. The polymerization temperature used was in the range of 60°C - 70°C . After addition, ageing was performed for approximately 2 hours and an adjustment was made to form the solid parts of 30% so as to produce a stable silica composite water-dispersible resin composition. The mean particle diameter was $0.052 \mu\text{m}$. Subsequently, 20 g of hexamethoxy methylol melamine (product of Mitsui Toatsu chemical Corp., product name: Saimel [phonetic] #350) was further added to 100 g of the above-mentioned water-dispersible solution produced and coating was performed onto a polished soft steel so as to form a dry film thickness of approximately 30 microns, and baking was performed at a temperature of 180°C for 40 min. The coated film produced was dipped in a warm water of 40°C for 7 days, but abnormalities such as whitening and swelling were not observed on the coated film.

Comparative example 1

(1) Ammonium phosphate of polyoxyethylene (17 mol adduct) alkyl ether 2 parts

- (2) α -olefin sodium sulfonate 0.5 parts
- (3) Deionized water 100 parts
- (4) Methyl methacrylate 134 parts
- (5) Ethyl acrylate 134 parts
- (6) N-methylol acryl amide 6 parts
- (7) Ammonium phosphate of polyoxyethylene (17 mol adduct) alkyl ether 4 parts
- (8) α -olefin sodium sulfonate 1.5 parts
- (9) Ludox AM (solid parts=30%) 60 parts
- (10) Deionized water 461.5 parts
- (11) Diammonium phosphate 0.5 parts
- (12) 5% potassium persulfate solution 20 parts
- (13) 2% sodium bisulfite solution 20 parts

Components (7)-(11) were charged to a reaction vessel saturated with a nitrogen gas ahead of time, heating was performed to 60°C, and emulsion monomer mixture of (1)-(6) and components (12) and (13) were dropwise added to the reaction vessel in 3 hours. The polymerization temperature used was in the range of 60°C-70°C. After addition, ageing was performed for approximately 2 hours and then, an adjustment was made to form the solid parts of 30% so as to produce a stable silica composite water-dispersible resin composition. The mean particle diameter was 0.12 μm .

[p. 7]

Furthermore, an adjustment was made for the non-volatile material to form 15% and coating was performed for a calcium silicate

plate at a ratio of approximately 100 g/m^2 , and drying was performed under $100^\circ\text{C} \times 10 \text{ min}$, and coating was performed with a commercial water-dispersible paint to form a thickness of 1 mm and drying was subsequently performed at room temperature for approximately 14 days. When measurement was performed for the adhesion, the adhesion achieved was low of 0.7 kg/cm .

Comparative example 2

- (1) polyoxyethylene (6 mol adduct) nonyl ether ammonium sulfate 2 parts
- (2) polyoxyethylene (20 mol adduct) nonyl phenyl ether 0.5 parts
- (3) Copper sulfate solution ($2 \times 10^{-4} \text{ mol/l}$ solution) 100 parts
- (4) Methyl methacrylate 136 parts
- (5) 2-ethyl hexyl acrylate 126 parts
- (6) 2,2,2-trifluoroethyl methacrylate 10 parts
- (7) Acrylic acid 3 parts
- (8) polyoxyethylene (6 mol adduct) nonyl ether ammonium sulfate 6 parts
- (9) polyoxyethylene (20 mol adduct) nonyl phenyl ether 1.5 parts
- (10) Ludox AM (solid parts=30%) 260 parts
- (11) Copper sulfate solution ($2 \times 10^{-4} \text{ mol/l}$ solution) 297 parts
- (12) Diammonium phosphate 0.5 parts
- (13) 5% potassium persulfate (Copper sulfate $2 \times 10^{-4} \text{ mol/l}$ solution) 20 parts
- (13) 2% sodium bisulfite (Copper sulfate $2 \times 10^{-4} \text{ mol/l}$ solution) 20 parts

Components (8)-(12) were charged to a reaction vessel saturated with a nitrogen gas ahead of time, heating was performed to 60°C, and emulsion monomer mixture of (1)-(7) and components (13) and (14) were dropwise added to the reaction vessel in 3 hours. The polymerization temperature used was in the range of 60°C-70°C. After addition, ageing was performed for approximately 2 hours and then, cooling was further performed and an adjustment was made to form the pH in the range of 8-9 with an aqueous ammonia, and the solid parts of 40% so as to produce a stable silica composite water-dispersible resin composition. The mean particle diameter was 0.07 μm . Furthermore, an adjustment was made for the non-volatile material to form 15% and coating was performed for a calcium silicate plate at a ratio of approximately 100 g/m², and drying was performed under 100°C x 10 min, and coating was performed with a commercial water-dispersible paint to form a thickness of 1 mm and drying was subsequently performed at room temperature for approximately 14 days. When measurement was performed for the adhesion, the adhesion achieved was low of 0.5 kg/cm.

Comparative example 3

- (1) Dioctyl sulfosuccinate 6 parts
- (2) α -olefin sodium sulfonate 3 parts
- (3) Copper sulfate solution (2 x 10⁻⁷ mol/l solution) 220 parts
- (4) Butyl methacrylate 276 parts
- (5) FM0711 10 parts

- (6) N-n-butoxy methyl acryl amide 5 parts
(7) 5% potassium persulfate (Copper sulfate 2×10^{-7} mol/l solution) 20 parts
(8) 2% sodium bisulfite (Copper sulfate 2×10^{-7} mol/l solution) 20 parts

Components (1)-(3) were charged to a reaction vessel saturated with a nitrogen gas ahead of time, heating was performed to 60°C, and emulsion monomer mixture of (4)-(6) and components (7) and (8) were dropwise added to the reaction vessel in 3 hours. The polymerization temperature used was in the range of 60°C-70°C. After addition, ageing was performed for approximately 2 hours and then, an adjustment was made to form the solid parts of 30% so as to produce a stable silica composite water-dispersible resin composition. The mean particle diameter was 0.05 μm . Furthermore, an adjustment was made for the non-volatile material to form 15% and coating was performed for a calcium silicate plate at a ratio of approximately 100 g/m², and drying was performed under 100°C x 10 min, and coating was performed with a commercial water-dispersible paint to form a thickness of 1 mm and drying was subsequently performed at room temperature for approximately 14 days. When measurement was performed for the adhesion, the adhesion achieved was low of 0.4 kg/cm.

Comparative example 4

- (1) Dioctyl sulfosuccinate 6 parts
(2) α -olefin sodium sulfonate 3 parts

- (3) Copper sulfate solution (2×10^{-7} mol/l solution) 660 parts
- (4) Methyl methacrylate 138 parts
- (5) Butyl acrylate 138 parts
- (6) N-n-butoxy methyl acryl amide 5 parts
- (7) 5% potassium persulfate (Copper sulfate 2×10^{-7} mol/l solution) 20 parts
- (8) 2% sodium bisulfite (Copper sulfate 2×10^{-7} mol/l solution) 20 parts

Components (1)-(3) were charged to a reaction vessel saturated with a nitrogen gas ahead of time, heating was performed to 60°C , and emulsion monomer mixture of (4)-(6) and components (7) and (8) were dropwise added to the reaction vessel in 3 hours. The polymerization temperature used was in the range of 60°C - 70°C . After addition, ageing was performed for approximately 2 hours and then, an adjustment was made to form the solid parts of 30% so as to produce a stable silica composite water-dispersible resin composition.

[p. 8]

The mean particle diameter was $0.06 \mu\text{m}$. Subsequently, 20 g of hexamethoxy methylol melamine (product of Mitsui Toatsu chemical Corp., product name: Saimel [phonetic] #350) was further added to 100 g of the above-mentioned water-dispersible solution produced and coating was performed onto a polished soft steel so as to form a dry film thickness of approximately 30 microns, and baking was performed at a temperature of 180°C for 40 min. When coated film produced was dipped in a warm water of 40°C for 7 days,

abnormalities such as whitening and swelling were observed on the coated film.

Applicant: Toyo Ink Mfg. Co.

//cont. from the front page//

[p. 9]

Amendments

Requested: November 28, 1989

[Translator's note: The requested amendments are incorporated into the text of this translation.]

[p.]

[Translator's note: text on last page is not related to the above document]

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cc: K. Gironda
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